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Study of mechanical degradation of UHMWPE acetabular components due to clinical X-ray procedures

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Abstract The use of multi-component femoral implants to replace the femur head and re-establish bone motion has been widespread since the 70s. Frequently these implants have spherical metallic heads made of, for example, 316-L stainless steel or Cr–Co alloys, which allow rotational motion towards a polymeric component (UHMWPE). One of the major causes of implant rejection is the generation of UHMWPE debris on the surface between the implant head and the polymeric component. The gamma ray sterilization of implants and the periodical X-ray medical control could contribute to premature degradation of the polymeric surface, resulting in increased wear and shortened lifetime of the implant. In this work we study the degradation degree of the polymeric UHMWPE component as function of the X-ray dose. The elasto-plastic deformation and recovery were carried out by means of a nanohardness tester equipment and the polymer degradation was measured using a fast Fourier transform infra-red (FT-IR) equipment. The results show the compromise among the irradiation doses, the surface oxidation and the mechanical properties of the samples.

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Introduction

Ultra-high molecular weight polyethylene (UHMWPE) is the polymer of choice as the bearing material in hip and knee joint replacements mostly because of its resistance to wear, high strength and low frictional coefficient [1–9]. An UHMWPE molecule consists of numerous repeating units of ethylene monomers. The backbone structure of the molecule is the C–C covalent bond. The UHMWPE molecules are arranged in both ordered and disordered regions, i.e., crystalline and amorphous respectively. In the crystalline region, the chains are folded with the chain axis. The area of the fold interface is much larger than the chain fold length, which generates a lamellar shape characteristic for each crystallite. In the amorphous region, there is no regular chain folding, but adjacent chains which are interconnected through random mechanical entanglements and occasionally chemical crosslinks [1, 8]. The connections between crystalline and amorphous regions are provided by tie molecules. The balance between crystalline and amorphous regions, the number and kind of tie molecules, the number and nature of connections within the amorphous region, i.e., the degree of mechanical entanglements and crosslinks, and the presence or absence of orientation of the crystallites determine the mechanical properties of UHMWPE [1, 10].

Gamma irradiation has been used to sterilize orthopedic components, but it also alters the chemical structure of the polymer. During the irradiating process, hydrogen is stripped from the carbon backbone, leaving free radicals which can persist for years in biological environment. Free radicals may react with oxygen as it diffuses into the polymer from the surroundings by breaking the carbon backbone, leaving carbonyl groups on the new ends of the chain fragments, compromising the polymer's high molecular weight [11]. In addition to oxidative scission, radicals may also be consumed through cross-linking, which occurs when the free radicals are able to react one to another instead of create links between chains. When oxidation occurs as a result of sterilization, the mechanical properties of the material are adversely affected, including lower ductility and lower strength [2, 6] and a decreased wear resistance [7]. This deterioration can result in increased introduction of wear debris into the joint space, eventually leading to osteolysis and loosening of the acetabular component [3]. Crosslinking on the other hand eliminates free radicals before they oxidize, improving the wear performance of the polymer [5].

One can see in the literature a lot of papers explaining the damage induced in the polymers structure by bombardment with high energies (>500 keV) and doses (>25 kGy) of gamma rays and ions [1–10, 12–15] and recently, Buncick et al. [16] have mentioned damage of polymers by low x-ray dose in XPS measurements.

During the surgery procedure to replace a femoral head, the patients are exposed to low energy X-ray fluoroscopy (80–100 keV) in order to find the correct functional position of the implant. Sometimes this procedure can spend several hours and the polymer is in contact with atmospheric air during the x-ray exposure. After the surgery several clinical x-ray examinations must be made periodically in order to observe the implant status and functionality. Both medical examinations, fluoroscopy and clinical x-rays, take place with the polymeric component in contact with an oxygen-rich interface, the atmospheric air and the synovial liquid respectively. The presence of oxygen in contact with the polymer surface during x-ray exposure can promote the oxidation of the free-radicals compromising the polymer mechanical behavior [11, 17].

In this study, UHMWPE samples that have been exposed to clinical low energy x-ray and fluoroscopy (80 keV) will be analyzed in order to determine how the clinical procedure affects the extent of oxidation and crosslinking. In addition, nanohardness and Young modulus depth profile measurements will show the mechanical damage degree of the samples as function of depth and exposition time.

Experimental methods

Materials and processing

To develop this work, we used a commercial UHMWPE sample supplied by a prosthetic industry. Polymer from a 40 mm diameter rod was cut into disks 10 mm thick, to represent a typical thickness of the acetabular cups used in total hip replacements. The disks were cut into six pieces that were polished using sandpaper from grade 100 to 4,000. After the polishing procedure, the specimens were cleaned in isopropyl alcohol ultrasound bath.

Five samples were irradiated with X-rays in air, at room temperature using a digital clinical equipment, model Siemens Polidoros-80. The distance between the emission tube and the sample was kept constant at 50 cm and the applied voltage (kV_p) was 80 kV. The set of samples studied in this work was exposed during 3, 6, 9, 12, and 15 min. irradiation periods at fluence of 100 mGy min^{-1}.

Sample characterization

All the specimens were tested using a Fischerscope HV100 nanohardness equipment with the intention to assess the mechanical properties of the polymeric materials. The instrumented hardness tests were performed using a Berkovich indenter based on dynamical load–unload cycles during a total period of 2 min for each, providing a variety of information about the sample as hardness, elastic modulus, elastic–plastic behavior, among others. At least 10 valid measurements were carried out for each sample, with at least 300 μm distant of each other.

Fourier Transform Infrared Spectroscopy (FT-IR) was carried out with the purpose of analyzing possible changes in hydrogen–carbon bonds, and polymer oxidation and crosslinking. All infrared spectra were obtained using a Perkin-Elmer Spectrum One spectrometer in the range of 4,000–650 cm^{-1} by the attenuated total reflection (ATR) technique, with a horizontal ATR device. Fifty scans were taken with 4 cm^{-1} resolution. The software provided by the equipment treated all the infrared spectra. The level of oxidation, defined as oxidation index (OI), was determined by the ratio of the peak areas which contains the carboxyl (800–1,300 cm^{-1}) and carbonyl (2,700–3,000 cm^{-1}) groups relative to the area associated with methylene groups (1,450–1,480 cm^{-1}) as presented by Lee et al. [18].

The influence of the oxidation index with the mechanical changes determined by the indentation method was studied according to the ASTM standards as described in Burroughs & Blanchet and in the ASTM D 2765 [19, 20].

Scanning electron microscopy (SEM) was used to analyze the polymer surface morphology and the degradation of the surface quality by increase of roughness by breaking the lamellar structure. The samples exposed with X-ray were coated with gold and the micrographs were made using a Philips XL-30 equipment operating at 20 kV.

Results and discussion

Figure 1 shows the ATR–FT-IR spectra of the samples irradiated with 80 kV X-ray and the sample as polished (control). One can see that the oxidation index (OI)

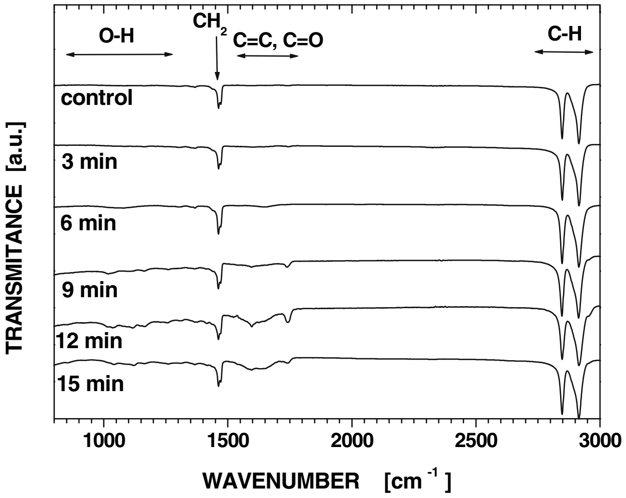

Fig. 1 ATR–FT-IR spectra of the UHMWPE samples irradiated with 80 kV X-ray using a fluoroscopy equipment. The exposition times were 3, 6, 9, 12, and 15 min

increases with the exposition time, especially at the carboxyl bonds (800–1300 cm^{-1}). The presence of crosslink C=C (1,640 cm^{-1}) and the oxidation at the end of the polymer chains, C=O (1,550–1,850 cm^{-1}), also increases with the irradiation time ($t > 9$ min) but the conversion of free radicals into crosslink bonds is smaller than the oxidation process. The ATR–FT-IR technique measures solid samples only near the surface where the oxidation process takes place and the crosslink formed at deeper regions of the polymer was not computed in the spectra.

In the same way, the mechanical properties of the samples are affected by the surface oxidation as shown in Fig. 2. The Young modulus (Fig. 2a) and the hardness (Fig. 2b) of the samples decrease with the x-ray dose, mostly for the region near the surface. The measurements at 1.5 μm show a reduction of hardness (18%) and elastic modulus (20%). In a deeper region (26 μm), this effect is reduced to 4% of hardness and 2% of elastic modulus, showing a degradation of the polymer at the region near to the oxygen atmosphere due to the X-ray irradiation.

The mechanical properties measured reflect the oxidation generated by the X-ray irradiation, increasing the defects on the polymer surface, which become more fragile. This is evinced by the elastic modulus behavior, which shows low values at 5 μm, indicating an increasing of the surface brittleness, probably with a very thin thickness. The achievement of higher depth values revealed a toughness increase, which explain the decrease of the hardness values and increase of the elastic modulus values after exceed the defected region. The surface alteration detected plays an important role on instrumented hardness assays, revealing hardening of the sample surface.

These results were confirmed by the micrographs displayed on Fig. 3, which shows the micrographs of the UHMWPE surface for the sample without irradiation and for the samples irradiated with X-ray during 6 and 15 min. The micrographs indicate an increase of the surface roughness showing the polymer chain ends emerging out of the surface exposing the UHMWPE lamellar structure. This results confirm the worsening of the mechanical properties and the increase of the C=O and O–H bonds near the surface indicated by the hardness and ATR-FTIR tests. These results also show that the presence of polymer debris in the human tissue near the prosthetic implant may be generated by the surface deterioration due to the X-ray clinical examination.

Conclusions

The samples irradiated with X-ray at low energy and doses show clearly that the sample hardness decreases with the exposition time and with the polymer oxidation degree.

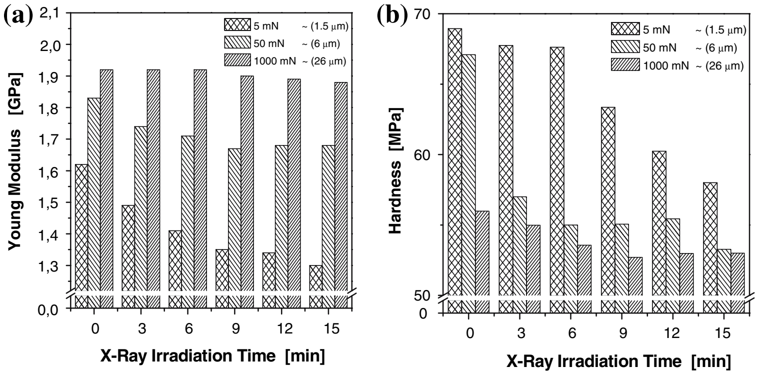

Fig. 2 (**a**) Young modulus and (**b**) hardness obtained with a nanoindenter using a berkovich tip for the UHMWPE samples irradiated with 80 kV X-ray as function of the exposition time. The maximum load and depth of testing were 5 mN (~1.5 μm), 50 mN (~6 μm), and 1000 mN (~26 μm)

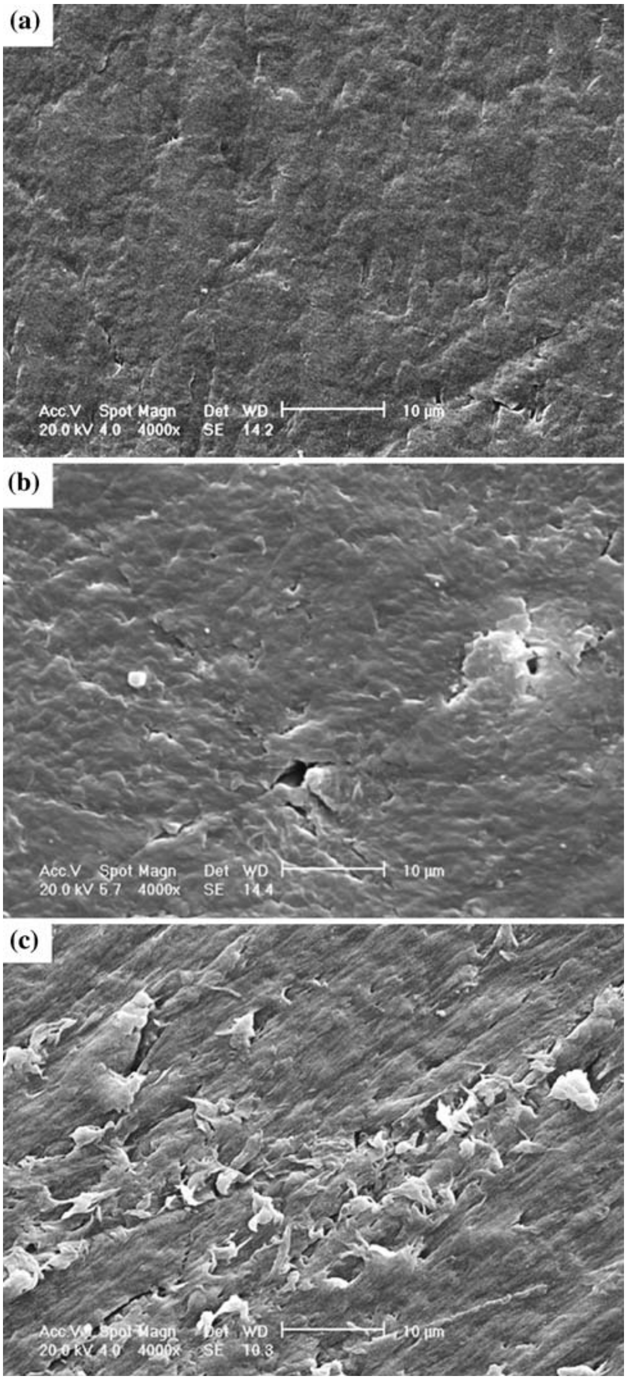

Fig. 3 Scanning electron micrographs at 20 kV and 4000 X magnification of the UHMWPE samples as polished without exposition (**a**), and irradiated during 6 min (**b**) and 15 min (**c**) with 80 kV X-ray using a fluoroscopy equipment

The samples oxidation occurs also at deeper layers because the x-ray photons can traverse all the sample thickness and the oxygen atom range, due to diffusion during exposition, can reach some micrometers.

The FT-IR spectra show an increase of the oxidation index with the exposition time, i.e., an increase of the O–H, C=O and C=C chemical bonding and a reduction of the CH_2 peak that is typical of the surface oxidation process. The oxidation effect can be clearly observed for the last tree samples (time > 9 min), and correlated with the strong reduction of the sample hardness in the near surface region. The surface deterioration showed by SEM micrographs exposing the polymer lamellar structure and the presence of chain ends can also be explained by the C=O bonds that only occur at the polymer chain end, resulting an increase in roughness and, consequently hardness decrease.

These results shows that, also with a clinical X-ray procedure, the surface of the polymeric component can be damaged and the production of debris must be investigated as function of the number of X-ray procedures of the patients up to the revision surgery. All the X-ray expositions were made in air, but the same behavior is expected when the UHMWPE are immersed in a synovial liquid environment. Patients that needs scintillography and radiotherapy procedures that uses high X-ray and gamma doses also must be carefully investigated.

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References

1. R. L. CLOUGH, *Nucl. Instrum. Methods Phys. Res. B: Beam Inter. Mater. Atoms* **185** (2001) 8
2. J. P. COLLIER, D. K. SPERLING, J. H. CURRIER, L. C. SUTULA, K. A. SAUM and M. B MAYOR, *J. Arthroplasty*, **11**(4) (1996) 377
3. M. JASTY and W. H. HARRIS, *Adv. Oper. Orthop.* **1** (1993) 1
4. H. MCKELLOP, F. W. SHEN, B. LU, P. CAMPBELL and R. SALOVEY, *J. Orthop. Res.* **17** (1999) 157
5. O. K. MURATOGLU, C. R. BRAGDON, D. O. O'CONNOR, M. JASTY and W. H. HARRIS, *Proc. 45th Ann. Meeting Orthop. Res. Soc.* **817** (1999)
6. L. C. SUTULA, J. P. COLLIER, K. A. SAUM, B. H. CURRIER, J. H. CURRIER, W. M. SANFORD, M. B. MAYOR, R. E. WOODING, D. K. SPERLING, I. R. WILLIAMS and D. J. KASPRZAK, *Clinical Orthop. Related Res.* **319** (1995) 28
7. K. S. TOOHEY, T. A. BLANCHET and D. D. HECKELMAN, *Wear* **255** (2003) 1076
8. K. WUNSCH and H. J. DALCOLMO, *Inter. J. Radiat. Appl. Instrumen.. Part C. Radiat. Phys. Chem.* **39**(5) (1992) 443
9. S. M. KURTZ, O. K. MURATOGLU, R. F. GSELL, W. SHEN, C. F. COOPER, J. BUCHANAN, S. SPIEGELBERG, S. S. YAU and A. A. EDIDIN, *Proc. 45th Ann. Meeting Orthop. Res. Soc.*, **98** (1999)
10. A. WANG, A. ESSNER, V. K. POLINENI, C. STARK and H. H. DUMBLETON, *Tribol. Inter.* **31** (1998) 17
11. L. COSTA, M. P. LUDA, L. TROSSARELLI, E. M. B. PREVER, M. CROVA and P. GALLINARO, *Biomaterials* **19** (1998)
12. H. E. JOHNS, E. R. EPP, D. V. CORMACK and S. O. FEDORUK, *J.Radiol.* **25** (1952) 302

13. T. A. BLANCHET and B. R. BURROUGHS, *J. Biomed. Mater. Res.: Appl. Biomater.* **58**(6) (2001) 684
14. D. C. SUN, G. SCHMIDIG, C. STARK and J. H. DUMBLETON, *Proc. 21st Ann. Meeting Trans. Soc. Biomater.* **362** (1995)
15. V. PREMNATH, W. H. HARRIS, M. JASTY and E. W. MERRILL, *Biomaterials* **17** (1996) 1741
16. M. C. BUNCICK, D. E. THOMAS, K. S. MCKINNY and M. S. JAHAN, *Appl. Surf. Sci.* **156** (2000) 97
17. L. A. VASCONCELLOS, E. BLANDO and R. HÜBLER, Proc. III Congresso Latino Americano de Órgãos artificiais e Biomateriais (III COLAOB), CD, BR139, (2004)
18. A. W. LEE, J. P. SANTERRE and E. BOYNTON, *Biomaterials* **21** (2000) 851
19. B. R. BURROUGHS and T. A. BLANCHET, *Tribol. Trans.* **44**(2) (2001) 215
20. ASTM D 2765, *Annual Book of ASTM Standards* **8** (2001) 114